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Basaltic and Solution Reference Materials for Iron, Copper and Zinc Isotope Measurements

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Iron, Cu and Zn stable isotope systems are applied in constraining a variety of geochemical and environmental processes. Secondary reference materials have been developed by the Institute of Geology, Chinese Academy of Geological Sciences (CAGS), in collaboration with other participating laboratories, comprising three solutions (CAGS-Fe, CAGS-Cu and CAGS-Zn) and one basalt (CAGS-Basalt). These materials exhibit sufficient homogeneity and stability for application in Fe, Cu and Zn isotopic ratio determinations. Reference values were determined by inter-laboratory analytical comparisons involving up to eight participating laboratories employing MC-ICP-MS techniques, based on the unweighted means of submitted results. Isotopic compositions are reported in per mil notation, based on reference materials IRMM-014 for Fe, NIST SRM 976 for Cu and IRMM-3702 for Zn. Respective reference values of CAGS-Fe, CAGS-Cu and CAGS-Zn solutions are as follows: $\delta^{56}\text{Fe} = 0.83 \pm 0.06$ and $\delta^{57}\text{Fe} = 1.20 \pm 0.12$, $\delta^{65}\text{Cu} = 0.57 \pm 0.05$, and $\delta^{66}\text{Zn} = -0.79 \pm 0.12$ and $\delta^{68}\text{Zn} = -1.65 \pm 0.24$, respectively. Those of CAGS-Basalt are $\delta^{56}\text{Fe} = 0.15 \pm 0.05$, $\delta^{57}\text{Fe} = 0.22 \pm 0.05$, $\delta^{65}\text{Cu} = 0.12 \pm 0.07$, $\delta^{66}\text{Zn} = 0.17 \pm 0.11$, and $\delta^{68}\text{Zn} = 0.34 \pm 0.21$ (2s).

Keywords: reference materials, Fe isotopes, Cu isotopes, Zn isotopes, single-metal solution, basalt.

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High-precision analyses of stable Fe, Cu and Zn isotopes have been possible since the advent of multi-collector-inductively coupled plasma-mass spectrometry (MC-ICP-MS) (Maréchal *et al.* 1999, Zhu *et al.* 2000a, Belshaw *et al.* 2000, Anbar *et al.* 2001). With better understanding of their natural distribution and mass-fractionation mechanisms (Zhu *et al.* 2002, Dauphas *et al.* 2017, Moynier *et al.* 2017), these isotopic systems have been increasingly applied to constrain various parameters in many areas of science, including cosmochemistry (Zhu *et al.* 2000b, Luck *et al.* 2003), geochemistry (Zhu *et al.* 2002, Sossi *et al.* 2012, Zhang *et al.* 2015), mineral resources (Zhu *et al.* 2000a, Larson *et al.* 2003, Dong *et al.* 2017, Gao *et al.* 2018), oceanographic and environmental studies (Zhu *et al.* 2001, John and Adkins 2010, González *et al.* 2016), biology (Zhu *et al.* 2002, Moynier *et al.* 2009, Li *et al.* 2016), and medical science (Walczyk *et al.* 2002, Costas-Rodríguez *et al.* 2014, Larner *et al.* 2015). Recent reviews provide helpful references concerning these applications (Zhu *et al.* 2013, Dauphas *et al.* 2017, Moynier *et al.* 2017).

Iron has four naturally occurring stable isotopes, ^{54}Fe , ^{56}Fe , ^{57}Fe and ^{58}Fe , with natural abundances of 5.845%, 91.754%, 2.119% and 0.282%, respectively (Meija *et al.* 2016). Their isotopic compositions are expressed as $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$ values relative to the Institute for Reference Materials and Measurements (IRMM) RM IRMM-014 (Taylor *et al.* 1992), in per mil notation (‰), with $\delta^{56}\text{Fe}$ values in natural samples ranging from approximately -4 to +2 (Zhu *et al.* 2013, Dauphas *et al.* 2017). Cu has two naturally occurring stable isotopes, ^{63}Cu and ^{65}Cu , with abundances of 69.15% and 30.85%, respectively (Meija *et al.* 2016). Cu isotopic compositions are expressed relative to National Institute of Standards and Technology (NIST) reference material NIST SRM 976. Natural mass-dependent variations of terrestrial samples in $\delta^{65}\text{Cu}$ cover values from -16.5 to +10 (Zhu *et al.* 2013, Moynier *et al.* 2017). Zn has five naturally occurring stable isotopes, ^{64}Zn , ^{66}Zn , ^{67}Zn , ^{68}Zn and ^{70}Zn , with natural abundances of 49.17%, 27.73%, 4.04%, 18.45% and 0.61%, respectively (Meija *et al.* 2016). Zn isotopic compositions are usually expressed as $\delta^{66}\text{Zn}$ and $\delta^{68}\text{Zn}$ relative to measurement standards JMC Lyon or IRMM-3702 with the latter being applied here. Natural $\delta^{66}\text{Zn}$ values range from -1.49 to +1.12 (Zhu *et al.* 2013, Moynier *et al.* 2017).

Applications of these isotopic systems rely heavily on precise and accurate determinations of isotopic compositions, and reference materials play fundamental roles in analyses. Two types of reference material are required to ensure measurement reliability: (a) single-element reference solutions for instrument calibration; and (b) geochemical reference materials to assess quality of chromatographic separation, measurement procedures, and mass spectrometry performance, as well as being helpful for inter-laboratory comparisons. The pure materials IRMM-014, NIST SRM 976, JMC Lyon and IRMM-3702 have been used as single-element solutions, and are internationally accepted as “delta-zero” reference materials for Fe, Cu and Zn isotopes, respectively. IRMM-014, NIST SRM 976 and JMC Lyon have been largely discontinued and are difficult to acquire. Secondary (“non-delta-zero”) reference materials for Fe, Cu and Zn isotopic analyses are required for instrument calibration. Here we describe three secondary reference solutions prepared specifically for Fe, Cu and Zn isotopic analyses: CAGS-Fe, CAGS-Cu and CAGS-Zn.

For isotopic analyses of geochemical samples, reference materials with compositions similar to the samples are needed. Geochemical reference materials such as basalt (BCR-1, BCR-2, BHVO-1 and BIR-1(a)), peridotite (JP-1 and DTS-2(b)), andesite (AGV-2) and manganese nodules (NOD-P-1) have been employed as isotopic reference materials to check reliability of Fe, Cu and Zn isotopic data (e.g., Dauphas *et al.* 2004, Chapman *et al.* 2006, Dideriksen *et al.* 2006, Craddock and Dauphas, 2011, Moynier *et al.* 2011, Millet *et al.* 2012, Liu *et al.* 2014, Sossi *et al.* 2015, Chen *et al.* 2016). However, as for single-element solutions, these materials were prepared as reference materials for elemental composition measurements only, and not specifically for isotopic analyses. Although they are useful external indicators of data accuracy and method reproducibility, their isotopic homogeneities have not been thoroughly assessed. Internationally benchmarked geological reference materials for Fe, Cu and Zn isotopes are needed. Basalts are the main components of oceanic crust. They form at high temperatures and cool quickly, contain few accessory phases, and are relatively easy to digest. Here we report the development of a basalt reference material, CAGS-Basalt (“CAGSR” in previous publications (Zhao *et al.* 2010, Dong *et al.* 2017)) for Fe, Cu and Zn isotopic ratio measurements. Isotopic homogeneity and stability of CAGS-Basalt were tested rigorously and are sufficient for the material to be used as a valid reference material.

Isotopic compositions of CAGS-Fe, CAGS-Cu, CAGS-Zn and CAGS-Basalt have been precisely determined by an inter-laboratory comparison with eight laboratories for CAGS-Fe, six for CAGS-Cu, seven for CAGS-Zn, six for CAGS-Basalt-Fe, five for CAGS-Basalt-Cu and four for CAGS-Basalt-Zn.

Experimental

Apparatus and reagents

CAGS-Basalt was prepared in a Class 1000 clean room at the Laboratory of Isotopic Geology, Institute of Geology, Chinese Academy of Geological Sciences (CAGS), Beijing, China. CAGS-Fe, CAGS-Cu and CAGS-Zn solutions were prepared in Class 100 laminar flow hoods in this clean room. A Savillex[®] DST-1000 acid purification system was used to purify acids used, including HCl, HNO₃ and HF. Savillex[®] PFA containers, and FEP, HDPE and PP bottles, were soaked overnight in 5 mol l⁻¹ HNO₃ at ~ 100 °C, rinsed with water (resistivity 15 MΩ cm), soaked in 1.5 mol l⁻¹ purified HNO₃ overnight, and rinsed with pure water (resistivity 18.2 MΩ cm) three times, before final drying.

Preparation of candidate reference materials

The single-metal solutions (CAGS-Fe, CAGS-Cu and CAGS-Zn) were prepared from high-purity Fe, Cu and Zn reference solutions provided by the National Centre of Analysis and Testing for Nonferrous Metals and Electronic Materials, Beijing, China, with certified concentrations of 1000 µg ml⁻¹ in 1 mol l⁻¹ HNO₃. The Fe reference solution (1000 ml) was dispensed into 100 10 ml HDPE bottles and sealed for storage. Twenty 50 ml bottles of Cu and Zn reference materials (1000 µg ml⁻¹ in 1 mol l⁻¹ HNO₃, with identical batch numbers) were combined in a single 1000 ml FEP bottle. Homogeneity was ensured by shaking. About 100 ml of each mixed solution was diluted to 100 µg ml⁻¹ with 0.1 mol l⁻¹ HCl, dispensed into 100 10 ml HDPE bottles, and sealed for storage.

CAGS-Basalt reference materials were prepared from olivine basalt reference material GBW 07105 from Zhangjiakou, Hebei Province, China, provided by the Institute of Geophysical and Geochemical Exploration, CAGS. Iron, Cu and Zn contents of CAGS-Basalt are given in Table 1. Five bottles of GBW 07105 reference

material (200 mesh, 70 g in each bottle, identical batch numbers) were mixed in a FEP bottle. Homogeneity was ensured by shaking before the material was dispensed into 80 4 ml PP bottles and sealed for storage. These powders were used to test for isotopic homogeneity. The dispensed reference materials were stored at laboratory temperatures (22 ± 2 °C).

Digestion of isotopic reference materials

Basaltic reference materials BCR-2 and BIR-1(a) and CAGS-Basalt) were analysed for their Fe, Cu and Zn isotopic compositions. About 0.1 g of each was weighed accurately into 7 ml Savillex® beakers and heated on a hotplate at 130 °C with 5 ml of a 3:1 mixture of 17 mol l⁻¹ HF and 12 mol l⁻¹ HNO₃, to ensure complete dissolution. After digestion, the solutions were evaporated to dryness, redissolved in 12 mol l⁻¹ HNO₃, evaporated to dryness three times, dissolved in 9 mol l⁻¹ HCl, and evaporated to dryness three times. The residues were dissolved in 2 ml of 7 mol l⁻¹ HCl + 0.001% H₂O₂ and centrifuged for 5 min at 4000 rpm to remove any residual solid before chromatographic separation of Fe, Cu and Zn.

Chromatographic separation of Fe, Cu and Zn

The chemical purification method used is as described by Maréchal *et al.* (1999) and Zhu *et al.* (2002). Bio-Rad AG MP-1 anion-exchange resin (200–400 mesh; chloride form; 10 ml Poly-Prep® column) was used for separation of Fe, Cu and Zn from matrix elements. The resin was cleaned three times with alternating 1 mol l⁻¹ HCl and H₂O (18.2 MΩ cm). The filled column was washed three times with alternating 10 ml 0.5 mol l⁻¹ HNO₃ and H₂O (18.2 MΩ cm). The resin volume was adjusted to 1.6 ml, in 7 mol l⁻¹ HCl. The column was conditioned with 6 ml 7 mol l⁻¹ HCl + 0.001% H₂O₂, before a sample in 1 ml 7 mol l⁻¹ HCl + 0.001% H₂O₂ was loaded onto it. Matrix elements such as Na, Mg, Al, K, Ca, Ti, Cr, Ni and Mn were eluted in 10 ml 7 mol l⁻¹ HCl, leaving Fe, Co, Cu and Zn on the resin. Cu was eluted in the following 20 ml 7 mol l⁻¹ HCl + 0.001% H₂O₂. Fe was eluted with 20 ml 2 mol l⁻¹ HCl + 0.001% H₂O₂, and Zn with 10 ml 0.5 mol l⁻¹ HNO₃. Elution sequences are summarized in Table 2.

The Fe fraction was evaporated to dryness, dissolved in concentrated HNO₃, and then re-evaporated to dryness three times to remove all chloride, and re-dissolved in 0.1 mol l⁻¹ HNO₃ prior to isotopic analysis. The Cu fraction was evaporated to dryness, and re-dissolved in 0.1 mol l⁻¹ HCl. The Zn fraction was evaporated to dryness, dissolved in concentrated HCl, re-evaporated to dryness three times to remove all nitrate, and re-dissolved in 0.1 mol l⁻¹ HCl prior to isotopic analysis.

Total procedural blanks (from sample dissolution to mass spectrometry) were 0.001 µg for Cu, 0.09 µg for Fe, and 0.006 µg for Zn, with such amounts having no effect on δ values (approximate totals processed were Cu = 3 µg, Fe = 3000 µg and Zn = 10 µg). Recoveries of Cu, Fe and Zn were 99.5% \pm 0.8% (n = 3), 99.9% \pm 0.3% (n = 3), and 100.7% \pm 4.0% (n = 3), respectively.

MC-ICP-MS analysis

Iron, Cu and Zn isotopic compositions of the purified reference materials were determined using a Nu Plasma HR MC-ICP-MS, with variable dispersion ion optics and a fixed array of twelve Faraday collectors, at the MNR (Ministry of Natural Resources of the People's Republic of China) Key Laboratory of Isotopic Geology, Institute of Geology, CAGS. Isotopic mass fractionation was determined by standard-sample bracketing (Zhu *et al.* 2000, Belshaw *et al.* 2000). Iron isotopic ratios were determined in high-resolution mode ($M/\Delta M \sim 7000$), and Cu and Zn isotopic ratios in low-resolution mode ($M/\Delta M \sim 400$). ⁵⁴Cr may cause isobaric interference with ⁵⁴Fe, and ⁵⁴Cr was monitored at mass ⁵³Cr, but Cr was removed during the chromatographic separation, and thus no correction was necessary. There are no interferences on ⁶³Cu and ⁶⁵Cu, ⁶⁴Zn, ⁶⁶Zn, ⁶⁷Zn and ⁶⁸Zn. Each analysis involved ten cycles with an integration time of 10 s per cycle. The RF power was 1300 W. An ASX-100 automatic sampler and a Nu Instruments DSN-100 desolvating nebuliser were used. Samples and standards were diluted to produce solutions containing 200 ng ml⁻¹ Cu and Zn in 0.1 mol l⁻¹ HCl and 5 µg ml⁻¹ Fe solution in 0.1 mol l⁻¹ HNO₃ respectively. Prior to each analysis, sequential 100 s rinses with 1 mol l⁻¹ HCl or HNO₃ and 0.1 mol l⁻¹ HCl or HNO₃ of 100 s were performed.

The effect of acidity on instrumental mass discrimination was investigated earlier (Li *et al.* 2008), with results indicating that HNO₃ has significant effects on Cu and Zn isotopes, whereas no effect was observed with HCl at concentrations of 0.05–3 mol l⁻¹. HCl was therefore used for sample introduction.

Iron, Cu and Zn isotopic values relative to IRMM-014, NIST SRM 976 and IRMM-3702, respectively, were calculated as follows:

$$\delta^{56}\text{Fe} = \left(\frac{{}^{56}\text{Fe} / {}^{54}\text{Fe}_{\text{sample}}}{{}^{56}\text{Fe} / {}^{54}\text{Fe}_{\text{IRMM-014}}} - 1 \right) \times 1000 \quad (1)$$

$$\delta^{57}\text{Fe} = \left(\frac{{}^{57}\text{Fe} / {}^{54}\text{Fe}_{\text{sample}}}{{}^{57}\text{Fe} / {}^{54}\text{Fe}_{\text{IRMM-014}}} - 1 \right) \times 1000 \quad (2)$$

$$\delta^{65}\text{Cu} = \left(\frac{{}^{65}\text{Cu} / {}^{63}\text{Cu}_{\text{sample}}}{{}^{65}\text{Cu} / {}^{63}\text{Cu}_{\text{SRM 976}}} - 1 \right) \times 1000 \quad (3)$$

$$\delta^{66}\text{Zn} = \left(\frac{{}^{66}\text{Zn} / {}^{64}\text{Zn}_{\text{sample}}}{{}^{66}\text{Zn} / {}^{64}\text{Zn}_{\text{IRMM-3702}}} - 1 \right) \times 1000 \quad (4)$$

$$\delta^{68}\text{Zn} = \left(\frac{{}^{68}\text{Zn} / {}^{64}\text{Zn}_{\text{sample}}}{{}^{68}\text{Zn} / {}^{64}\text{Zn}_{\text{IRMM-3702}}} - 1 \right) \times 1000 \quad (5)$$

Results and discussion

Accuracy

Basaltic reference materials have the following isotopic compositions, BCR-2: $\delta^{56}\text{Fe} = 0.07 \pm 0.02$, $\delta^{65}\text{Cu} = 0.16 \pm 0.04$, $\delta^{66}\text{Zn} = -0.07 \pm 0.02$; and BIR-1(a): $\delta^{56}\text{Fe} = 0.04 \pm 0.03$, $\delta^{65}\text{Cu} = 0.03 \pm 0.02$, $\delta^{66}\text{Zn} = -0.09 \pm 0.03$ (2s).

These results are in good agreement with published data, within uncertainties (Figure 1 and online supporting information Table S1).

Homogeneity of reference materials

Homogeneity is of first-order importance for reference materials, and it was achieved here through application of national regulations for reference material preparation (ISO Guide 35, 2006). Thirteen bottles each of CAGS-Fe, CAGS-Cu and CAGS-Zn, and thirteen bottles of CAGS-Basalt were randomly selected to test homogeneity of mixed materials. Two subsamples were taken from each bottle, with each being treated as an independent sample. Results of isotopic analyses of the replicates are expressed as X_{i1} and X_{i2} in Tables 3 and 4, and the average of duplicate pairs by X_i . Homogeneity testing was conducted under strictly the same conditions, with all tests being conducted in a single laboratory, using the same analytical method, by one analyst, and with all samples tested in the same session.

Between-bottle inhomogeneity was tested by single-factor ANOVA statistics. The experimental F ratio is the ratio of the among-bottle variance (s_{among}^2) to the within-bottle variance (s_{within}^2):

$$F = \frac{s_{\text{among}}^2}{s_{\text{within}}^2} \quad (6)$$

where the s_{among}^2 is the ratio of among-bottle sums of squares (SS_{among}) to the associated among-bottle degrees of freedom (ν_{among}), and the s_{within}^2 is the ratio of within-bottle sums of squares (SS_{within}) to the associated within-bottle degrees of freedom (ν_{within}):

$$s_{\text{among}}^2 = SS_{\text{among}} / v_{\text{among}} \quad (7)$$

$$s_{\text{within}}^2 = SS_{\text{within}} / v_{\text{within}} \quad (8)$$

where v_{among} and v_{within} depend on the number of units from which samples are taken (m) and the number of replicate measurements for each bottle (n), with v_{among} and v_{within} computed as follows:

$$v_{\text{among}} = m - 1 \quad (9)$$

$$v_{\text{within}} = m \times n - m \quad (10)$$

Using Excel™, results shown in the ANOVA tables were computed (Tables 5 and 6). F -testing indicates that the result of homogeneity testing was insignificant ($1 < F < F_{\text{critical}}(v_{\text{among}}, v_{\text{within}})$; critical value of F for $\alpha = 5\%$; Kane *et al.* 2003), demonstrating that the samples have very good homogeneity. Differences in δ values (Tables 5 and 6) were caused mainly by the repeatability of the method, rather than inhomogeneity of the reference materials.

Stability of reference materials

The long-term stability of CAGS-Fe, CAGS-Cu, CAGS-Zn and CAGS-Basalt were evaluated by determining $\delta^{56}\text{Fe}$, $\delta^{57}\text{Fe}$, $\delta^{65}\text{Cu}$, $\delta^{66}\text{Zn}$ and $\delta^{68}\text{Zn}$ values over a seven-year period (Figures 2 and 3, Tables S2 and S3).

A linear model was used in evaluating stability, expressed as follows (ISO Guide 35 2006):

$$Y = b_0 + b_1 X + \varepsilon \quad (11)$$

where b_0 and b_1 are regression coefficients, ε denotes the random error component, X is time in months, and Y is the Fe, Cu, or Zn isotope ratio. The slope of the fitted line can be computed from the following expressions:

$$b_1 = \frac{\sum_{i=1}^n (X_i - \bar{X})(Y_i - \bar{Y})}{\sum_{i=1}^n (X_i - \bar{X})^2} \quad (12)$$

$$b_0 = \bar{Y} - b_1 \bar{X} \quad (13)$$

The standard deviation of a point along the line can be computed from s^2 and $s(b_1)$ as follows:

$$s^2 = \frac{\sum_{i=1}^n (Y_i - b_0 - b_1 X_i)^2}{n - 2} \quad (14)$$

$$s(b_1) = \frac{s}{\sqrt{\sum_{i=1}^n (X_i - \bar{X})^2}} \quad (15)$$

Using Equation (12) and an appropriate Student's t factor for $(n - 2)$ degrees of freedom, and $p = 0.95$ (95% level of confidence), we obtain $t_{0.95, n-2} = 2.0860$ for Fe in CAGS-Fe; 2.2010 for Cu in CAGS-Cu; 2.1788 for Zn in CAGS-Zn; 2.1009 for Fe in CAGS-Basalt; 2.3646 for Cu in CAGS-Basalt; and 2.2010 for Zn in CAGS-Basalt; with b_1 being tested for significance (ISO Guide 35 2006). As $|b_1| < t_{0.95, (n-2)} \cdot s(b_1)$, the slope was insignificant and no instability was observed (Tables S4 and S5). Results therefore indicate that over a seven-year period $\delta^{56}\text{Fe}$, $\delta^{57}\text{Fe}$, $\delta^{65}\text{Cu}$, $\delta^{66}\text{Zn}$ and $\delta^{68}\text{Zn}$ values for CAGS-Fe, CAGS-Cu, CAGS-Zn and CAGS-Basalt display no statistically significant instability.

Fe, Cu and Zn isotopic compositions of the reference materials

Reference isotopic compositions determined by inter-laboratory comparison with participating laboratories using different analytical approaches were consistent. For the intercomparison, CAGS-Fe, CAGS-Cu, CAGS-Zn and CAGS-Basalt samples were taken from different bottles for distribution. All materials were supplied as single samples. Three samples of each reference material were provided and laboratories were requested to analyse each sample three times. An overview of analytical protocols for each laboratory is provided in Table 7. Intercomparison results are given in Tables 8 and 9 and Figures 4 and 5, with data presented as means $\pm 2s$.

The consistency of inter-laboratory results confirms that the participating laboratories were able to perform accurate Fe, Cu and Zn isotope measurements. Iron, Cu and Zn isotopic compositions of the four reference materials were calculated from the unweighted means of inter-laboratory results, with results as follows.

$$\text{CAGS-Fe: } \delta^{56}\text{Fe} = 0.83 \pm 0.06, \delta^{57}\text{Fe} = 1.20 \pm 0.12$$

$$\text{CAGS-Cu: } \delta^{65}\text{Cu} = 0.57 \pm 0.05$$

$$\text{CAGS-Zn: } \delta^{66}\text{Zn} = -0.79 \pm 0.12, \delta^{68}\text{Zn} = -1.65 \pm 0.24$$

$$\text{CAGS-Basalt: } \delta^{56}\text{Fe} = 0.15 \pm 0.05; \delta^{57}\text{Fe} = 0.22 \pm 0.05; \delta^{65}\text{Cu} = 0.12 \pm 0.07;$$

$$\delta^{66}\text{Zn} = 0.17 \pm 0.11, \delta^{68}\text{Zn} = 0.34 \pm 0.21.$$

Conclusions

Three single-element solution reference materials and a basaltic reference material for Fe, Cu and Zn isotopic analyses were prepared. Their isotopic compositions were determined in participating laboratories by MC-ICP-MS. CAGS-Fe, CAGS-Cu and CAGS-Zn are satisfactory choices as reference materials for Fe, Cu and Zn isotopic analyses with their offset values from zero-delta, homogeneity, and stability being appropriate for

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application in instrument calibration and analyst training. CAGS-Basalt can be used to validate chromatographic separation and total measurement procedures, and in inter-laboratory comparisons. All these reference materials are available upon request from the Institute of Geology, CAGS.

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Supporting information

The following supporting information is available in the online version of this article:

Table S1. Iron, Cu and Zn isotopic compositions of reference materials BCR-2 and BIR-1(a).

Table S2. Long-term stability results for Fe, Cu and Zn isotopic compositions over 84 months.

Table S3. Long-term stability of Fe, Cu and Zn isotopic compositions of CAGS-Basalt.

Table S4. Results of stability tests for CAGS-Fe, CAGS-Cu and CAGS-Zn.

Table S5. Results of stability tests on CAGS-Basalt for Fe, Cu and Zn isotopes.

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Figure captions

Figure 1. Iron, Cu and Zn isotopic composition of BCR-2 and BIR-1(a) reported here and in referenced work.

Black diamonds represent BCR-2; black circles represent BIR-1(a); and red error bars represent 2s.

Figure 2. Long-term stability results of Fe, Cu and Zn isotopic compositions of CAGS-Fe, CAGS-Cu and

CAGS-Zn. Red error bars represent 2s.

Figure 3. Long-term stability of Fe, Cu and Zn isotopic compositions of CAGS-Basalt. Red error bars represent

2s.

Figure 4. Iron, Cu and Zn isotopic compositions of CAGS-Fe, CAGS-Cu and CAGS-Zn reference solutions, as

determined by participating laboratories. Blank circles represent the δ -value of replicates, black squares

represent averages, and red error bars represent 2s.

Figure 5. Iron, Cu and Zn isotopic compositions of CAGS-Basalt as determined by participating laboratories.

Blank circles represent the δ -value of replicates, black squares represent averages, and red error bars represent

2s.

Table 1.

Iron, Cu, and Zn contents of CAGS-Basalt

Element	Fe	Cu	Zn
Content	9.38% <i>m/m</i>	49 $\mu\text{g g}^{-1}$	150 $\mu\text{g g}^{-1}$

Table 2.

Elution sequence during ion-exchange chromatography

Eluent	Volume (ml)	Purpose
H ₂ O and 0.5 mol l ⁻¹ HNO ₃	8	Resin cleaning
7 mol l ⁻¹ HCl + 0.001% H ₂ O ₂	15	Resin conditioning
7 mol l ⁻¹ HCl + 0.001% H ₂ O ₂	1	Sample Load
7 mol l ⁻¹ HCl + 0.001% H ₂ O ₂	5	Matrix elution
7 mol l ⁻¹ HCl + 0.001% H ₂ O ₂	20	Cu elution
2 mol l ⁻¹ HCl + 0.001% H ₂ O ₂	22	Fe elution
0.5 mol l ⁻¹ HNO ₃	10	Zn elution

Table 3.

Results of isotopic homogeneity testing of CAGS-Fe, CAGS-Cu and CAGS-Zn

Bottle No.	$\delta^{56}\text{Fe}$			$\delta^{57}\text{Fe}$			$\delta^{65}\text{Cu}$			$\delta^{66}\text{Zn}$			$\delta^{68}\text{Zn}$		
	X_{i1}	X_{i2}	X_i	X_{i1}	X_{i2}	X_i	X_{i1}	X_{i2}	X_i	X_{i1}	X_{i2}	X_i	X_{i1}	X_{i2}	X_i
8	0.72	0.82	0.77	1.06	1.23	1.15	0.64	0.63	0.64	-0.82	-0.71	-0.76	-1.68	-1.3	-1.49
11	0.89	0.78	0.83	1.3	1.21	1.26	0.63	0.61	0.62	-0.74	-0.83	-0.79	-1.51	-1.64	-1.58
23	0.81	0.75	0.78	1.2	1.17	1.18	0.59	0.67	0.63	-0.89	-0.87	-0.88	-1.8	-1.72	-1.76
24	0.79	0.8	0.79	1.17	1.19	1.18	0.67	0.62	0.64	-0.85	-0.73	-0.79	-1.36	-1.38	-1.37
32	0.88	0.9	0.89	1.26	1.29	1.28	0.58	0.61	0.59	-0.77	-0.77	-0.77	-1.2	-1.54	-1.37
35	0.82	0.77	0.79	1.2	1.1	1.15	0.7	0.61	0.66	-0.9	-0.9	-0.9	-1.84	-1.9	-1.87
41	0.69	0.82	0.76	1.06	1.2	1.13	0.56	0.56	0.56	-0.86	-0.68	-0.77	-1.68	-1.19	-1.44
45	0.68	0.85	0.77	1.04	1.29	1.16	0.55	0.57	0.56	-0.84	-0.8	-0.82	-1.65	-1.61	-1.63
52	0.86	0.88	0.87	1.28	1.32	1.3	0.55	0.6	0.57	-0.95	-0.9	-0.92	-1.98	-1.84	-1.91
62	0.75	0.8	0.78	1.17	1.2	1.19	0.55	0.58	0.57	-0.82	-0.7	-0.76	-1.61	-1.22	-1.41
63	0.86	0.84	0.85	1.31	1.2	1.25	0.57	0.6	0.59	-0.89	-0.83	-0.86	-1.85	-1.66	-1.76
77	0.72	0.8	0.76	1.11	1.24	1.17	0.59	0.6	0.59	-0.71	-0.74	-0.72	-1.29	-1.39	-1.6
79	0.93	0.87	0.9	1.32	1.34	1.33	0.55	0.62	0.58	-0.81	-0.78	-0.79	-1.61	-1.56	-1.6

Long-term analysis of GAGS-Fe over seven years gave $\delta^{56}\text{Fe}$ of 0.82 ± 0.11 and $\delta^{57}\text{Fe}$ of 1.21 ± 0.15 (2s; $n = 734$) relative to IRMM-014.

Long-term analysis of GAGS-Cu over seven years gave $\delta^{65}\text{Cu}$ of 0.55 ± 0.08 (2s; $n = 289$) relative to NIST SRM 976.

Long-term analysis of GAGS-Zn over seven years gave $\delta^{66}\text{Zn}$ of -0.79 ± 0.11 and $\delta^{68}\text{Zn}$ of -1.59 ± 0.23 (2s; $n = 271$) relative to IRMM-3702.

Table 4.

Results of homogeneity testing of Fe, Cu and Zn isotopic compositions of CAGS-Basalt

Bottle No.	$\delta^{56}\text{Fe}$			$\delta^{57}\text{Fe}$			$\delta^{65}\text{Cu}$			$\delta^{66}\text{Zn}$			$\delta^{68}\text{Zn}$		
	X_{i1}	X_{i2}	X_i	X_{i1}	X_{i2}	X_i	X_{i1}	X_{i2}	X_i	X_{i1}	X_{i2}	X_i	X_{i1}	X_{i2}	X_i
8	0.07	0.07	0.07	0.07	0.07	0.07	0.16	0.08	0.12	0.26	0.24	0.25	0.51	0.47	0.49
11	0.14	0.11	0.13	0.13	0.12	0.13	0.23	0.13	0.18	0.30	0.31	0.31	0.58	0.65	0.62
23	0.12	0.14	0.13	0.17	0.14	0.16	0.24	0.25	0.25	0.23	0.23	0.23	0.49	0.44	0.46
24	0.10	0.09	0.10	0.11	0.21	0.16	0.19	0.32	0.26	0.22	0.25	0.23	0.41	0.50	0.45
32	0.08	0.15	0.12	0.19	0.01	0.10	0.21	0.07	0.14	0.25	0.19	0.22	0.51	0.36	0.43
35	0.07	0.02	0.05	0.18	0.11	0.15	0.30	0.15	0.23	0.22	0.25	0.23	0.42	0.53	0.48
41	0.14	0.15	0.15	0.08	0.08	0.08	0.15	0.13	0.14	0.21	0.29	0.25	0.37	0.57	0.47
45	0.14	0.02	0.08	0.11	0.16	0.14	0.18	0.20	0.19	0.30	0.27	0.29	0.55	0.46	0.50
52	0.10	0.16	0.13	0.15	0.11	0.13	0.25	0.16	0.21	0.28	0.29	0.28	0.55	0.60	0.58
62	0.14	0.13	0.14	0.05	0.06	0.06	0.13	0.10	0.12	0.28	0.29	0.29	0.48	0.57	0.53
63	0.08	0.08	0.08	0.18	0.17	0.18	0.31	0.28	0.30	0.28	0.27	0.28	0.56	0.51	0.54
77	0.09	0.11	0.10	0.11	0.15	0.13	0.18	0.24	0.21	0.22	0.32	0.27	0.39	0.63	0.51
79	0.09	0.07	0.08	0.06	0.13	0.10	0.12	0.14	0.13	0.25	0.28	0.26	0.50	0.55	0.53

Long-term analysis of GAGS-Fe over seven years gave $\delta^{56}\text{Fe}$ of 0.82 ± 0.11 and $\delta^{57}\text{Fe}$ of 1.21 ± 0.15 (2s; $n = 734$) relative to IRMM-014.

Long-term analysis of GAGS-Cu over seven years gave $\delta^{65}\text{Cu}$ of 0.55 ± 0.08 (2s; $n = 289$) relative to NIST SRM 976.

Long-term analysis of GAGS-Zn over seven years gave $\delta^{66}\text{Zn}$ of -0.79 ± 0.11 and $\delta^{68}\text{Zn}$ of -1.59 ± 0.23 (2s; $n = 271$) relative to IRMM-3702.

Table 5.

ANOVA table for homogeneity testing of Fe, Cu and Zn isotopic compositions of CAGS-Fe, CAGS-Cu and CAGS-Zn

CAGS	$\delta^{65}\text{Cu}$	$\delta^{56}\text{Fe}$	$\delta^{57}\text{Fe}$	$\delta^{66}\text{Zn}$	$\delta^{68}\text{Zn}$
n	2				
m	13				
SS_{among}	0.028	0.0645	0.1011	0.0918	0.7993
SS_{within}	0.0135	0.046	0.0799	0.0458	0.5025
ν_{among}	12				
ν_{within}	13				
F	2.24	1.52	1.37	2.17	1.72
$F_{0.05}(12, 13)$	2.6				

Table 6.

ANOVA table for homogeneity testing of Fe, Cu and Zn isotopic compositions of CAGS-Basalt

CAGS-Basalt	$\delta^{65}\text{Cu}$	$\delta^{56}\text{Fe}$	$\delta^{57}\text{Fe}$	$\delta^{66}\text{Zn}$	$\delta^{68}\text{Zn}$
n	2				
m	13				
SS_{among}	0.022	0.0326	0.0786	0.0175	0.0619
SS_{within}	0.0139	0.0296	0.0451	0.0125	0.0839
V_{among}	12				
V_{within}	13				
F	1.71	1.19	1.89	1.51	0.8
$F_{0.05}(12, 13)$	2.6				

Table 7.

Overview of the methods employed by participating laboratories for Fe, Cu and Zn isotopic analyses. The chromatographic procedures for Fe, Cu and Zn

Instrument parameter	Isotopic Geology, Institute of Geology, Chinese Academy of Sciences	Environments, University of Science and Technology of China	Earth Sciences, University of Science and Technology of China	Earth Sciences, University of Science and Technology of China	Earth Sciences, University of Science and Technology of China	Earth Sciences, University of Science and Technology of China	Earth Sciences, University of Science and Technology of China	Earth Sciences, University of Science and Technology of China	Earth Sciences, University of Science and Technology of China
Chromatography and sample introduction	Wang <i>et al.</i> (1999) and Zhu <i>et al.</i> (2015)	Chen <i>et al.</i> (2016)	Liu <i>et al.</i> (2014)	Wang <i>et al.</i> (1999) and Zhu <i>et al.</i> (2015)	Wang <i>et al.</i> (1999) and Zhu <i>et al.</i> (2015)	Wang <i>et al.</i> (1999) and Zhu <i>et al.</i> (2015)	Wang <i>et al.</i> (1999) and Zhu <i>et al.</i> (2015)	Zhu <i>et al.</i> (2015)	
Instrument (MC-ICP-MS)	Nu Plasma HR	Thermo Finnigan Neptune	Thermo Finnigan Neptune	Nu Plasma (Cu and Zn) and Thermo Finnigan Neptune	Thermo Finnigan Neptune	Nu Plasma HR	Nu Plasma HR	Thermo Finnigan Neptune	Thermo Finnigan Neptune
Sample introduction	Nu Instruments DSN-100	Cetac Aridus	Cetac Aridus	Nu Instruments DSN-100 (Fe) and Thermo Finnigan Neptune MCN 6000 (Cu and Zn)	Cetac Aridus	Nu Instruments DSN-100	Nu Instruments DSN-100	Wet Plasma	Cetac Aridus
Instrumental mass bias correction	SSB	SSB	SSB	SSB	SSB	SSB	SSB	SSB	SSB
Cup configuration	Cr: L3, ⁵⁶ Fe: H5 and ⁶³ Cu: H1 and ⁶⁵ Cu: H3 ⁶⁶ Zn: C, ⁶⁷ Zn: H3 and ⁶⁸ Zn: H3	Cr: L1, ⁵⁷ Fe: H1, ⁵⁸ Fe: H2 and ⁶³ Cu: L4 and ⁶⁵ Cu: L2 C, ⁶⁷ Zn: H1, ⁶⁸ Zn: H1		Cr: L3, ⁵⁶ Fe: H5 and ⁶³ Cu: H1 and ⁶⁵ Cu: H3 ⁶⁶ Zn: C, ⁶⁷ Zn: H3 and ⁶⁸ Zn: H3	⁵⁴ Fe (⁸⁴ Cr): L2, ⁵⁶ Fe: L1 and ⁵⁷ Fe: C ⁶³ Cu: C and ⁶⁵ Cu: H1 ⁶⁴ Zn: L1, ⁶⁶ Zn: H1, ⁶⁷ Zn: H2 and ⁶⁸ Zn: H3	Cr: L7, ⁵⁶ Fe: H1 and ⁶³ Cu: L7 and ⁶⁵ Cu: H3 ⁶⁶ Zn: H1, ⁶⁷ Zn: H2 and ⁶⁸ Zn: H3	(⁵⁴ Cr): L3, ⁵⁶ Fe: H4 and ⁶³ Cu: L2 and ⁶⁵ Cu: H3 ⁶⁶ Zn: C, ⁶⁷ Zn: H3 and ⁶⁸ Zn: H3	⁵³ Cr: L2, ⁵⁴ Fe (⁵⁴ Cr): L1, ⁵⁶ Fe: C, ⁵⁷ Fe: H1, ⁵⁸ Fe: H2 and ⁶⁰ Ni: H4	e (⁵⁴ Cr): L1, ⁵⁶ Fe: C, ⁵⁷ Fe: H1, ⁵⁸ Fe: H2 and ⁶⁰ Ni: H4
Resolution mode	Fe: MR (~7000) Cu and Zn: LR	Fe: MR (>6000) Cu and Zn: LR	Zn: LR	Fe: HR (~7000) Cu and Zn: LR	Fe: MR (>7000) Cu and Zn: LR	Fe: HR (~7000) Cu and Zn: LR	Fe: HR (~7000) Cu and Zn: LR	Fe: MR (7000)	Fe: MR (>7000)
RF Power (W)	1300	1125–1200	1250	1300	1200	1300	1350	1200	1200
Cones	Ni cone	Ni cone	Ni cone	Ni cone	X cone	Ni cone	Ni cone	Ni cone	Ni cone
Sample uptake	~ 100 µl min ⁻¹	~ 50 µl min ⁻¹	~ 50 µl min ⁻¹	100 µl min ⁻¹	~ 100 µl min ⁻¹	~ 100 µl min ⁻¹	~ 100 µl min ⁻¹	~ 50 µl min ⁻¹	~ 50 µl min ⁻¹
⁵⁶ Fe sensitivity	~ 4 V/ppm	~ 9 V/ppm		~ 4 V/ppm	~ 130 V/ppm	~ 4 V/ppm	~ 4 V/ppm	~ 8 V/ppm	~ 6 V/ppm
⁶³ Cu sensitivity	~ 30 V/ppm	~ 20 V/ppm		~ 30 V/ppm	~ 250 V/ppm	~ 30 V/ppm	~ 30 V/ppm		
⁶⁴ Zn sensitivity	~ 30 V/ppm	~ 25 V/ppm	~ 15 V/ppm	~ 30 V/ppm	~ 250 V/ppm	~ 30 V/ppm	~ 30 V/ppm		
Blocks	1	1	3	1	1	1	1	3	9
Cycles/Block	10	60	25	20	50	30	10	10	10
Integration Time	10 s	2.097 s	~8 s	10 s	4.194 s	30 s	20 s	4.194 s	4.194 s

Table 8.

Iron, Cu and Zn isotopic compositions of CAGS-Fe, CAGS-Cu and CAGS-Zn reference solutions, as determined by participating laboratories

Institution/laboratory	Replicates	$\delta^{56}\text{Fe} \pm 2s$	$\delta^{57}\text{Fe} \pm 2s$	$\delta^{65}\text{Cu} \pm 2s$	$\delta^{66}\text{Zn} \pm 2s$	$\delta^{68}\text{Zn} \pm 2s$
MNR Key Laboratory of Isotopic Geology, Institute of Geology, CAGS	1	0.8	1.2	0.59	-0.87	-1.77
	2	0.87	1.17	0.6	-0.81	-1.7
	3	0.84	1.22	0.58	-0.78	-1.65
	Mean $\pm 2s$	0.84 \pm 0.07	1.20 \pm 0.05	0.59 \pm 0.02	-0.82 \pm 0.09	-1.71 \pm 0.12
CAS Key Laboratory of Crust-Mantle and Environments, University of Science and Technology of China	1	0.77	1.11	0.52	-0.84	-1.74
	2	0.79	1.18	0.54	-0.83	-1.73
	3	0.8	1.19	0.53	-0.83	-1.71
	Mean $\pm 2s$	0.79 \pm 0.03	1.16 \pm 0.09	0.53 \pm 0.02	-0.83 \pm 0.01	-1.73 \pm 0.03
Isotope Geochemistry Lab, China University of Geosciences, Beijing	1				-0.88	-1.69
	2				-0.9	-1.79
	3				-0.87	-1.68
	Mean $\pm 2s$				-0.88 \pm 0.03	-1.72 \pm 0.12
Department of Earth Sciences, University of Oxford	1	0.79	1.15	0.55	-0.7	-1.52
	2	0.82	1.3	0.6	-0.71	-1.57
	3	0.84	1.18	0.55	-0.79	-1.54
	Mean $\pm 2s$	0.82 \pm 0.05	1.21 \pm 0.16	0.57 \pm 0.06	-0.74 \pm 0.10	-1.54 \pm 0.05
Department of Earth and Environmental Sciences, Open University	1	0.88	1.27	0.59	-0.76	-1.2
	2	0.85	1.26	0.6	-0.76	-1.13
	3	0.87	1.3	0.58	-0.82	-1.21
	Mean $\pm 2s$	0.87 \pm 0.03	1.28 \pm 0.04	0.59 \pm 0.02	-0.78 \pm 0.07	-1.55 \pm 0.09
State Key Laboratory of Marine Environmental Science, Xiamen University	1	0.86	1.23	0.54	-0.82	-1.75
	2	0.85	1.22	0.62	-0.77	-1.81
	3	0.91	1.35	0.55	-0.83	-1.88
	Mean $\pm 2s$	0.87 \pm 0.06	1.27 \pm 0.14	0.57 \pm 0.09	-0.80 \pm 0.06	-1.81 \pm 0.13

First Institute of Oceanography, State Oceanic Administration of China, National Marine Environmental Monitoring Center	1	0.84	1.1	0.55	-0.72	-1.45
	2	0.79	1.08	0.55	-0.72	-1.49
	3	0.8	1.14	0.55	-0.77	-1.54
	Mean \pm 2s	0.81 \pm 0.05	1.10 \pm 0.06	0.55 \pm 0.00	-0.74 \pm 0.06	-1.49 \pm 0.09
State Key Laboratory for Mineral Deposits Research, Department of Earth Sciences, Nanjing University	1	0.81	1.21			
	2	0.83	1.19			
	3	0.84	1.18			
	Mean \pm 2s	0.83 \pm 0.03	1.19 \pm 0.03			
MNR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, CAGS	1	0.79	1.18			
	2	0.8	1.18			
	3	0.82	1.2			
	Mean \pm 2s	0.80 \pm 0.03	1.19 \pm 0.02			
GRAND MEAN \pm 2s		0.83 \pm 0.06	1.20 \pm 0.12	0.57 \pm 0.05	-0.79 \pm 0.12	-1.65 \pm 0.24

Table 9.

Iron, Cu and Zn isotopic compositions of CAGS-Basalt determined by participating laboratories

Institution/laboratory	Replicates	$\delta^{56}\text{Fe} \pm 2s$	$\delta^{57}\text{Fe} \pm 2s$	$\delta^{65}\text{Cu} \pm 2s$	$\delta^{66}\text{Zn} \pm 2s$	$\delta^{68}\text{Zn} \pm 2s$
MLR Key Laboratory of Isotopic Geology, Institute of Geology, CAGS	1	0.11	0.16	0.07	0.18	0.37
	2	0.13	0.22	0.13	0.24	0.47
	3	0.17	0.26	0.09	0.27	0.54
	Mean $\pm 2s$	0.14 \pm 0.05	0.21 \pm 0.11	0.10 \pm 0.06	0.23 \pm 0.09	0.46 \pm 0.17
CAS Key Laboratory of Crust-Mantle and Environments, University of Science and Technology of China	1	0.14	0.21	0.08	0.08	0.21
	2	0.17	0.27	0.1	0.12	0.23
	3	0.18	0.27	0.1	0.12	0.21
	Mean $\pm 2s$	0.16 \pm 0.04	0.25 \pm 0.06	0.09 \pm 0.02	0.11 \pm 0.04	0.21 \pm 0.02
Department of Earth Sciences, University of Oxford	1	0.13	0.17	0.14	0.12	0.22
	2	0.15	0.16	0.06	0.19	0.46
	3	0.09	0.26	0.1	0.09	0.18
	Mean $\pm 2s$	0.12 \pm 0.06	0.20 \pm 0.10	0.10 \pm 0.09	0.13 \pm 0.10	0.27 \pm 0.30
Department of Earth and Environmental Sciences, The Open University	1	0.15	0.28	0.15	0.25	0.48
	2	0.22	0.3	0.18	0.19	0.38
	3	0.15	0.2	0.21	0.22	0.39
	Mean $\pm 2s$	0.18 \pm 0.08	0.26 \pm 0.10	0.18 \pm 0.06	0.22 \pm 0.06	0.42 \pm 0.11
First Institute of Oceanography, State Oceanic Administration of China, National Marine Environmental Monitoring Centre	1	0.14	0.24	0.12		
	2	0.15	0.19	0.13		
	3	0.08	0.15	0.09		
	Mean $\pm 2s$	0.12 \pm 0.07	0.19 \pm 0.09	0.11 \pm 0.04		
State Key Laboratory for Mineral Deposits Research, Department of Earth Sciences, Nanjing University	1	0.14	0.28			
	2	0.15	0.19			
	3	0.21	0.23			
	Mean $\pm 2s$	0.17 \pm 0.04	0.23 \pm 0.05			
GRAND MEAN $\pm 2s$		0.15 \pm 0.05	0.22 \pm 0.05	0.12 \pm 0.07	0.17 \pm 0.11	0.34 \pm 0.21









